THE PREPARATION OF NITROSYL CYANIDE, ONCN, AND 8 ISOTOPIC SPECIES

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SUMMARY

Preparations of milligram quantities (3-5 mg) of nitrosyl cyanide, ONCN, 4 single and 4 double labelled species are described. Infrared frequencies are reported for identification purposes. The stability of ONCN is discussed. In contrast to reports in literature no explosions have occurred during any part of our work.

Key Words: Nitrosyl cyanide, IR frequencies.

INTRODUCTION

Nitrosyl cyanide, ONCN, is of importance both in preparations (1) and in theory (2) due to its weak central N-C bond with a dissociation energy of ca. 30 kcal mol^{-1} (3). It has earlier been prepared as described in (1), (4), and (5). Explosions during purification are reported (5). Ref. (4) reports rotational constants, B and C, of ONCN, $O^{15}NCN$,

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$ON^{13}CN$, and $ONC^{15}N$ based on microwave work. Ref. (5) reports the IR spectrum of gaseous ONCN (4000-200 cm^{-1}) with a suggested force field.

The purpose of this work was to establish a method of producing 3-5 mg quantities of ONCN and a number of isotopically enriched species without risking explosions. The species produced were characterized by their gas phase IR spectra.

EXPERIMENTAL

Preparation of unlabelled ONCN

$$ONCl \xrightarrow{AgCN} ONCN \qquad (1)$$

Preparation and purification of all intermediate and final products took place in evacuated systems avoiding the use of mercury manometers. Ca. 10 mmol ONCl was prepared according to (6):

$$2NO_2 + KCl \longrightarrow ONCl + KNO_3 \qquad (2)$$

NO_2 was obtained from commercial $Pb(NO_3)_2$ following (7) except for a final distillation from one trap at -80°C to another at -196°C to exclude H_2O etc. ONCl was purified by distillation at -80°C, p=2.8 Torr (L.K.B. gauge). The over-all yield of ONCl with respect to $Pb(NO_3)_2$ is ca. 50%.

2.70 g (20 mmol) commercial AgCN (Pierce Inorganic) was placed in a 15 ml. reaction vessel and dried in vacuo under heating (T≈90°C). By short immersion of the vessel into a bath at -196°C 0.01 mmol ONCl was condensed onto AgCN.

Then the vessel temperature was quickly raised to -30°C and magnetic stirring started. After 5 minutes at -30°C (pressure ca. 10 Torr (5)) a mixture of gaseous ONCN and unreacted ONCl was condensed in a connecting trap at -196°C. In separate experiments we showed that neither longer nor shorter reaction periods improved the yield of ONCN. The procedure described was repeated 9 times bringing a total of 0.1 mmol ONCl in contact with 20 mmol AgCN. ONCN was separated from unreacted ONCl and other impurities by repeated bulb to bulb distillations from a pentane slush bath (-130°C) to a bath at -196°C (5). At -130°C the vapour pressures of ONCN and ONCl are 0.2 Torr and 0.06 Torr (L.K.B. gauge), respectively. An average of 5 distillations produced ca. 0.05 mmol ONCN of sufficient purity for the present purpose (< 2% ONCl). In essence less than ca. 2% of the applied AgCN has reacted.

Preparation of labelled ONCN

$ONC^{15}N$ and $ON^{13}CN$

In separate preparations $AgC^{15}N$ (from aqueous solutions of 0.5 g (10 mmol) 99.5% enriched $NaC^{15}N$ (Stohler) and a slight excess (10.5 mmol) of $AgNO_3$) and $Ag^{13}CN$ (from 1.0 g (20 mmol) 90% enriched $Na^{13}CN$ (Merck)) were washed 5 times with distilled water followed by decantation and 5 times with ethyl alcohol (decantation) before drying in vacuo at T≈90°C.

Proceeding as above the expected quantities of 99.5% enriched $ONC^{15}N$ (ca. 3 mg) and 90% enriched $ON^{13}CN$ (ca. 3 mg) were obtained.

Infrared gas-phase frequencies are reported in Table 1.

Table 1 Infrared band centre frequencies (cm^{-1}) recorded at T≈40°C (inside)[a] and p≈10 Torr. Cell length 10 cm.

	ν_1	ν_2	ν_3	ν_4	%[c]
ONCN	2170.0[b]	1501.0[b]	820.0	588.5[b]	100
$ONC^{15}N$	2140.5	1500.8	818.5	584.4	99
$ON^{13}CN$	2122.0	1500.5	810.2	580.9	90
$O^{15}NCN$	2169.2	1476.1	807.3	585.1	95
$^{18}ONCN$	2169.0	1463.0	818.5	587.8	30
$O^{15}N^{13}CN$	2120.6	1475.3	797.9	578.7	85
$O^{15}NC^{15}N$	2140.4	1475.6	804.7	579.8	95
$^{18}ON^{13}CN$	2121.6	1462.3	809.3	581.3	27
$^{18}ONC^{15}N$	2140.4	1462.4	(816.5)[d]	(591.2)[d]	30

a To be discussed.
b In disagreement with (5).
c Enrichment.
d Two superimposed bands.

Again ca. 98% of $AgC^{15}N$ and $Ag^{13}CN$ was recovered to be used for preparation of double labelled species.

$O^{15}NCN$

2.0 g (25 mmol) 95.2% $NH_4{}^{15}NO_3$ (Merck) was dissolved in 7 ml H_2O and 2 ml concentrated H_2SO_4. $H^{15}NO_3$ and H_2O was distilled off in vacuo at room temperature onto 3 g (≈12.5 mmol) commercial PbO. Under slight heating and stirring an aqueous solution of $Pb(^{15}NO_3)_2$ was afterwards produced and the water removed in vacuo. $Pb(^{15}NO_3)_2$ was finally dried in vacuo at T≈200°C (7). Then we proceeded as already described:

$$Pb(^{15}NO_3)_2 \xrightarrow{400^\circ C} {}^{15}NO_2 \xrightarrow{KCl} O^{15}NCl \xrightarrow{AgCN} O^{15}NCN \qquad (3)$$

The total yield of $O^{15}NCl$ was 3 mmol (~200 mg). 0.1 mmol of this was used for the preparation of $O^{15}NCN$, while the rest was saved for preparations of double labelled species.

$^{18}ONCN$

1 ℓ (42 mmol) 60 atom % $^{18}O_2$ (Stohler) was reacted with a slight excess of NO (8) at room temperature to give 84 mmol 30 % $N^{18}O_2$. Excess of NO was removed by pumping (-196°C bath), finally purifying $N^{18}O_2$ by bulb (-80°C) to bulb (-196°C) distillations. Then we proceeded as already described:

$$N^{18}O_2 \xrightarrow{KCl} {}^{18}ONCl \xrightarrow{AgCN} {}^{18}ONCN \qquad (4)$$

The total yield of $^{18}ONCl$ was ca. 20 mmol of which 0.1 mmol was used to produce ca. 3 mg 30% enriched $^{18}ONCN$. The

remaining $^{18}ONCl$ was stored for use in preparations of double labelled species.

$O^{15}N^{13}CN$, $O^{15}NC^{15}N$, $^{18}ON^{13}CN$, and $^{18}ONC^{15}N$

$$Ag^{13}CN \xrightarrow{O^{15}NCl} O^{15}N^{13}CN \qquad (5)$$

$$AgC^{15}N \xrightarrow{O^{15}NCl} O^{15}NC^{15}N \qquad (6)$$

$$Ag^{13}CN \xrightarrow{^{18}ONCl} {}^{18}ON^{13}CN \qquad (7)$$

$$AgC^{15}N \xrightarrow{^{18}ONCl} {}^{18}ONC^{15}N \qquad (8)$$

The excess labelled $Ag^{13}CN$ and $AgC^{15}N$ applied in the preparations of $ON^{13}CN$ and $ONC^{15}N$ were purified prior to use in (5) - (8) by dissolving 2-3 g of the appropriate labelled AgCN in boiling 12M NH_4OH (ca. 10 ml). Slow cooling to $0^{\circ}C$ produced almost quantitative yields of crystalline $Ag^{13}CN$ and $AgC^{15}N$, respectively. After separation by decantation and washing with water and ethyl alcohol as usual the crystals were dried in vacuo at $T \approx 90^{\circ}C$ before use.

Table 1 reports infrared band centre frequencies of all the prepared species.

ONCN STABILITY

Gas phase ONCN is stable for 30 minutes (4) in a microwave copper cell at $T \approx -80^{\circ}C$ and $p \approx 50$ mTorr. When infrared spectra were recorded (Table 1) using a glass cell with KBr windows practically no deterioration was seen after 30 minutes at ca. 40° (inside temperature). After 1 hour a

ca. 10% decrease in observed band intensities was noted. Following sample condensation (-196°C) fractionation in vacuo at -130°C showed a minor (~0.2 Torr) increase of initial equilibrium pressure possibly due to NO. Sample purity was restored after one distillation.

Deep-blue ONCN in a quantity necessary to produce a pressure of 1 atm. at room temperature in a sealed-off NMR tube (i.d. 4 mm) converts quickly to a yellow solid substance while freely heating from -196°C to 20°C.

In the gas phase at room temperature ONCN reacts rapidly with Hg.

Explosions have never occurred during any of our experiments.

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